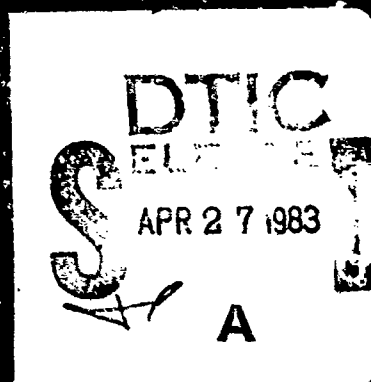


UCLA School of Engineering and Applied Science

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PREPARATION AND PROPERTIES OF HALIDE
GLASSES AND GLASS-POLYMER COMPOSITES

J.D. Mackenzie

Grant No. AFOSR 80-0059

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FINAL TECHNICAL REPORT

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

on project entitled

"PREPARATION AND PROPERTIES OF HALIDE GLASSES
AND GLASS-POLYMER COMPOSITES"

Grant No.: AFOSR 80-0059

Inclusive Dates: October 1, 1979 to September 30, 1982

Principal Investigator: Dr. John D. Mackenzie
Professor of Engineering and Applied Science

November, 1982

UCLA-ENG-82-19

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
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ABSTRACT

Research has been carried out on two families of solids. The first one involves fluoride, chloride and bromide glasses. The second one involves microporous silica glass impregnated with organic polymers as well as inorganic crystals. The viscosity, vibrational spectra, chemical durability, fiber preparation and effects on oxygen on the properties of fluorozirconates have been studied. A number of new halide glasses were discovered. Microporous silica glass impregnated with PMMA was found to be highly transparent in the visible and possesses abnormal properties. Many crystals impregnated into silica glass were found to have their melting points depressed and some crystallographic transitions were also suppressed.

I. Introduction

Inorganic glasses have been scientifically studied and practically utilized for a long time. The scientific challenge is due primarily to the fact that structurally, glasses resemble liquids but that mechanically, they behave like solids. One of the most important uses of inorganic glasses arises from their transparency in the visible and hence their fabrication into windows and lenses. This project is concerned with research on two relatively new families of glasses which are both transparent in the visible. The first group are glasses based on halides, especially fluorides. Most of these glasses are transparent from the UV to the IR. The second group are composites based on the impregnation of organic polymers and other materials into microporous silica glass.

At the commencement of this program in October 1979, small scale experiments had already been carried out at UCLA which showed that the preparation of these new transparent solids was feasible. During this reporting period, from October 1979 to September 1982, a great deal of work has been carried out. The progress made to date on these two types of glasses are summarized separately below.

II. Research on Halide Glasses

A. Background Information.

Almost all halide glasses reported in the literature prior to 1975 were based on $\text{BeF}_2^{(1)}$. Because of the very low refractive index of BeF_2 ($n_D = 1.275$), the so-called fluoroberyllate glasses also have low refractive indices

and have been considered for potential applications in high-power laser systems.⁽²⁾ BeF_2 has often been described as a structural analog of SiO_2 ⁽³⁾. BeF_2 glass has a three-dimensional random network structure in which BeF_4 tetrahedra are the basic building units with adjacent neighbors sharing only one corner similar to SiO_2 glass.⁽⁴⁾ Addition of alkali fluorides tends to break up the network and non-bridging fluorine ions are formed. However, the basic building units remain to be the BeF_4 tetrahedra. BeF_2 -based glasses are considered toxic materials and their preparation and handling are relatively difficult.

Another halide which forms glass readily is ZnCl_2 ⁽⁵⁾. Some binary glasses based on ZnCl_2 have also been reported⁽⁶⁾. However, these are very easily soluble in water. In 1975, Poulain et al. reported the successful preparation of some new fluoride glasses based on ZrF_4 ⁽⁷⁾. These new glasses are much more chemically durable than ZnCl_2 but are non-toxic. They are somewhat more transmitting in the IR than the fluoroberyllates. Because crystalline compounds of fluorides and molten fluorides containing zirconium have ZrF_6 polyhedra with x ranging from 6 to 8, it has been postulated that the structures of these new fluorozirconate glasses must be very different from that of silicates and fluoroberyllates⁽⁸⁾. In the case of oxides and fluoroberyllates, ease of glass-formation has always been associated with small coordination numbers of the network formers. For instance the coordination numbers for Si, Ge and Be are 4 and that for B is 3 and 4. The coordination number of Zr in ZrF_4 is 8.

In 1979, preliminary experiments carried out at UCLA showed that besides ZrF_4 , many other halide mixtures could form glass fairly easily. These

include mixtures based on $\text{AlF}_3\text{-CaF}_2$, $\text{HfF}_4\text{-BaF}_2$ and $\text{ZrF}_4\text{-NaCl}$. Since glass-formation appeared to be widespread among systems which were not toxic, since the structures of halide glasses were practically unknown, and since their optical transmissions promised to be superior to that of known oxide glasses in the infrared, there were strong justifications to perform research on new halide glasses.

B. Research Progress in this Period

1. Viscosity of Fluorozirconate Melts

The viscosity of liquids is governed by the structure at any temperature. Since glass is a supercooled liquid, viscosity information has a direct bearing on structure. Secondly, the ease of a liquid to form glass is directly governed by viscosity and the variation of viscosity with temperature. Thus for scientific and practical reasons, a study of the viscosity of molten fluoro-zirconates is important. During this period, a high temperature viscometer has been modified and viscosity measurements have been made on many molten fluoro-zirconates. Figure 1 shows the typical variation of viscosity with temperature for fluoro-zirconates. The common Arrhenius equation is not obeyed. It seems likely that the degree of "polymerization" increases with decreasing temperatures, as found for many associated liquids. The absolute values of viscosity are somewhat higher than that for fused salts like NaCl but are much less than that for glass-forming liquids like SiO_2 and B_2O_3 (See Table 1) for comparison). The degree of association is thus not extensive. From viscosity measurements, it may be postulated that the melt, and hence the glass, consists of ZrF_x anions and M^+ cations. The ZrF_x anions contain both

Table 1. Viscosity of fluorozirconate melts, other glass-forming liquids and molten salts at their liquidus temperature.

Substance	Structural type	T_m (°C)	Viscosity (Poises)	Activation Energy (Kcal/mol)	Reference
SiO ₂	3-dimensional	1710	10 ⁷	180	1
B ₂ O ₃	3-dimensional	540	>10 ⁵	>100	2
B ₂ O ₃	layer	450	10 ⁵	40	3
P ₂ O ₅	layer	572	>10 ⁵	41.5	4
ZnCl ₂	layer	318	50	40	5
Li ₂ SiO ₃	chain	1200	4	24	1
NaPO ₃	chain	615	17	16.5	6
LiBeF ₃	chain	365	5.6	14	7
NaCl	ionic	800	0.015	9.3	8
KNO ₃	ionic	337	0.03	4.3	8
BaZr ₂ F ₁₀		590	0.6	16.1	present
30BaF ₂ 10LaF ₃ 60ZrF ₄		540	3	25	present

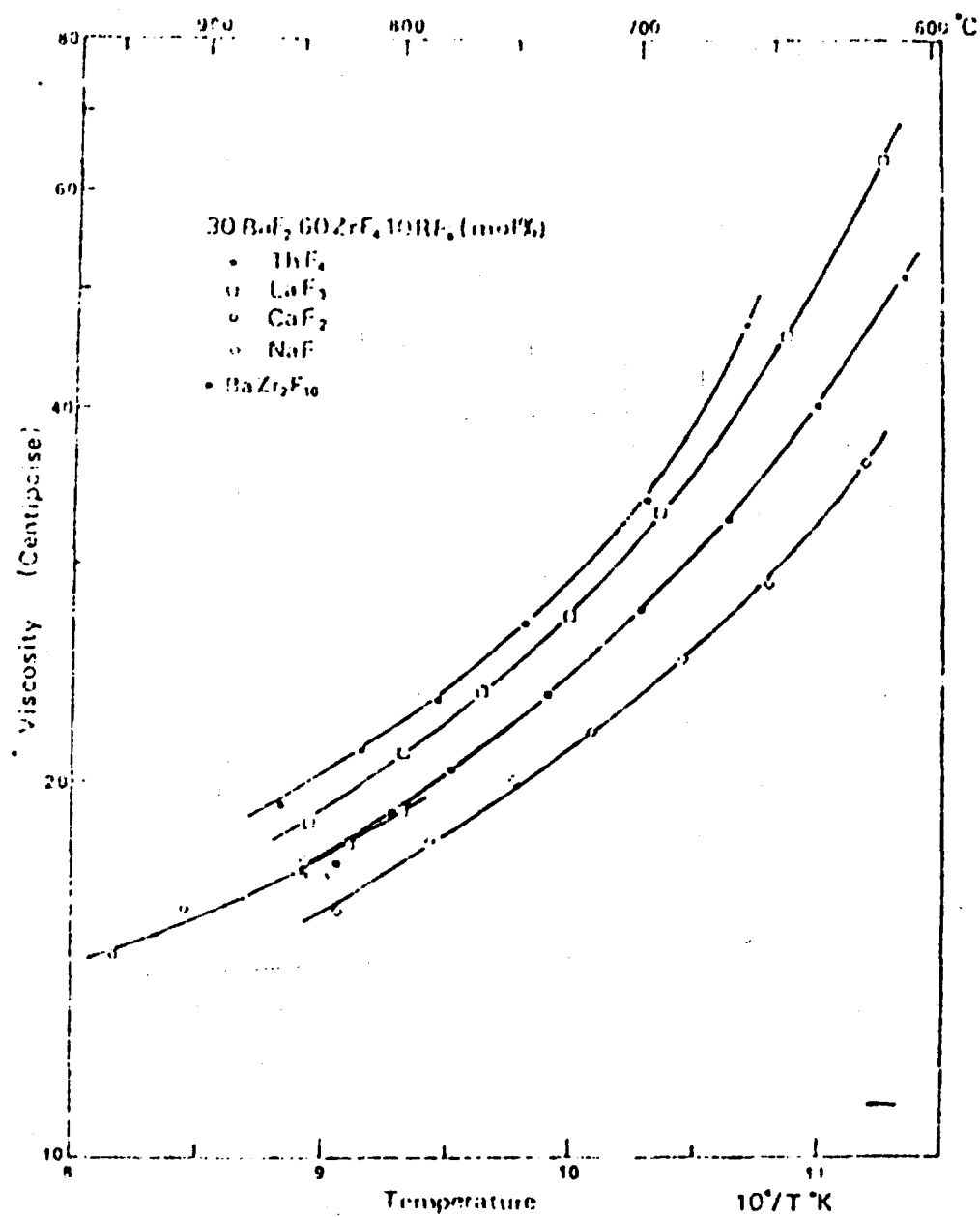


Figure 1. The effects of addition of NaF, CaF₂, LaF₃ and ThF₄ on the viscosity of a BaZr₂F₁₀ melt.

bridging and non-bridging fluorine ions. Viscosity values at the liquidus temperatures are low (less than 1 poise in general) and hence rapid quenching must be accepted for glass-formation for most fluorozirconates.

2. Chemical Durability in Water

The chemical durability of glasses in the system $\text{ZrF}_4\text{-BaF}_2\text{-ThF}_4$ has been studied at 20° , 30° and 40°C . The results of weight loss as functions of time, infrared transmission as functions of time, chemical compositions of glass and solutions as functions of time were combined with electron microscopy results in order to fully understand the corrosion mechanisms. The fundamental process seems to be the replacement of particular cations in the glass by positive ions from the water, with the probability of participation of water molecules. The corrosion appears to follow a $(\text{time})^{1/2}$ relation and is thus diffusion controlled. It was possible to relate the weight loss to the concentration of water in the glasses shown in Figure 2.

Chemical analysis results indicated that selective leaching of Ba^{2+} ions had occurred together with some Zr^{4+} ions while Th^{4+} ions remained in the glassy network. The loss of Ba^{++} ions seemed to have led to contraction of the glass surface and subsequent fracture. Thus even in moist atmospheres, unprotected fluoride glass surface can become weakened and lead to subsequent mechanical failure. In general, fluorozirconates were found to be much less chemically durable than silicate glasses such as window glass but could be superior to fluoroberyllates.

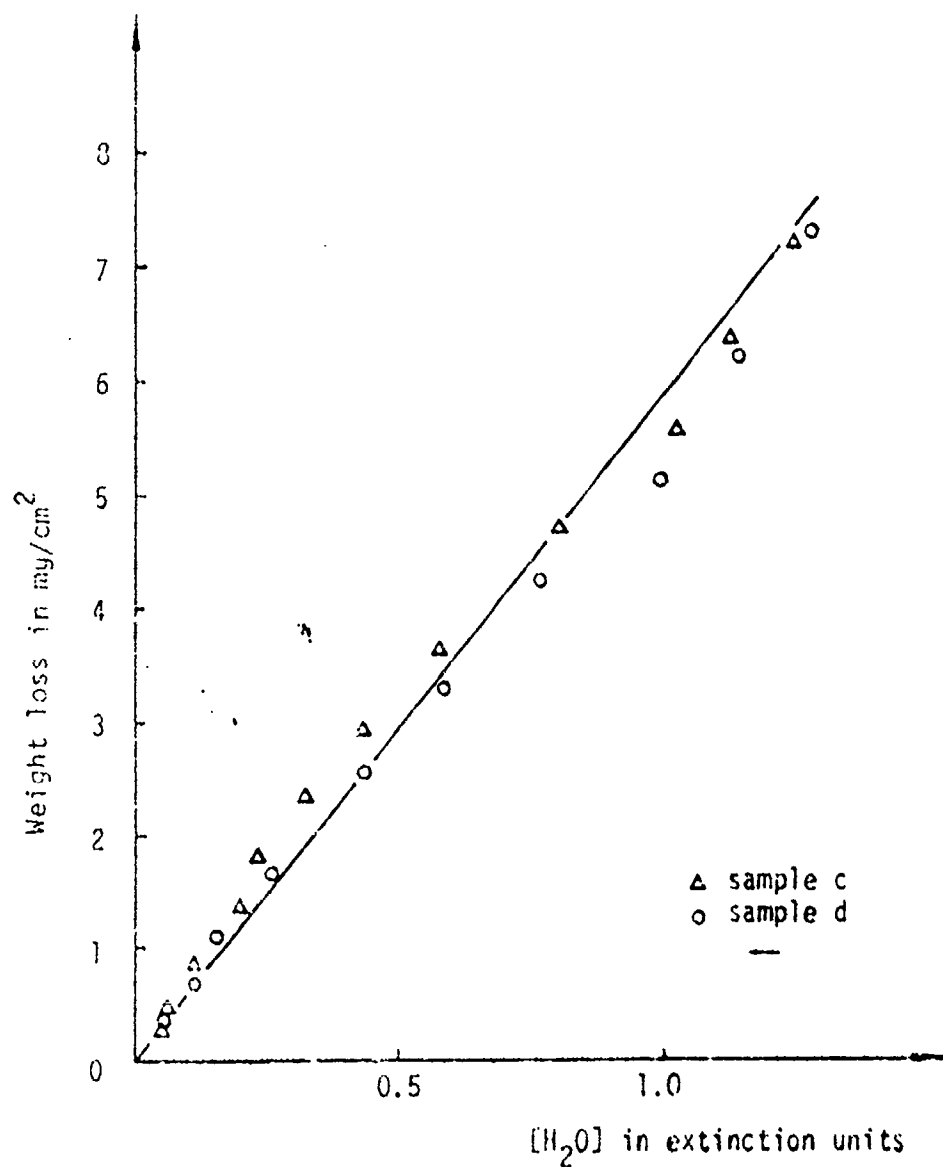


Figure 2. Weight loss versus water concentration in the surface of glasses leached in water at 30°C.

3. Vibrational Spectra and Structure

The infrared and Raman spectra of a large number of fluorozirconates and chloro-fluorozirconates were studied. Typical infrared and Raman spectra are shown in Figures 3 and 4 respectively. By correlating the spectra of the glass with those of crystalline and molten fluorozirconates, we have tentatively concluded that the basic building unit in these glasses is the ZrF_6 octahedra. In Figure 5, these octahedra are seen to form a six-membered ring. Adjacent rings in the glass structure are linked together via non-bridging fluorine ions and Ba^{2+} ions. For chloro-fluorozirconate glasses, the present interpretation of the results of vibrational spectra suggests the larger Cl ions to be the bridging ions as shown in Figure 6. The structures postulated involved relatively small ZrF_x chains or rings and are consistent with the viscosity results obtained.

4. New Halide Glasses

A number of new chloro-fluorozirconate glasses were prepared. The chemical compositions are shown in Table 2 together with the glass transition temperatures and crystallization temperatures.

New chloride and new bromide glasses have also been discovered. The system $NaCl-KCl-ThCl_4$ was found to have extensive regions of glass formation as shown in Figure 7. Some of these glasses are transparent to 14μ in the infrared. New glasses were also prepared based on $ZnBr_2$. The optical transmission of one of these bromide glasses in the infrared is shown in Figure 8. The chemical durabilities of the chloride and bromide glasses were inferior to those of the fluorides. For practical applications, all these new

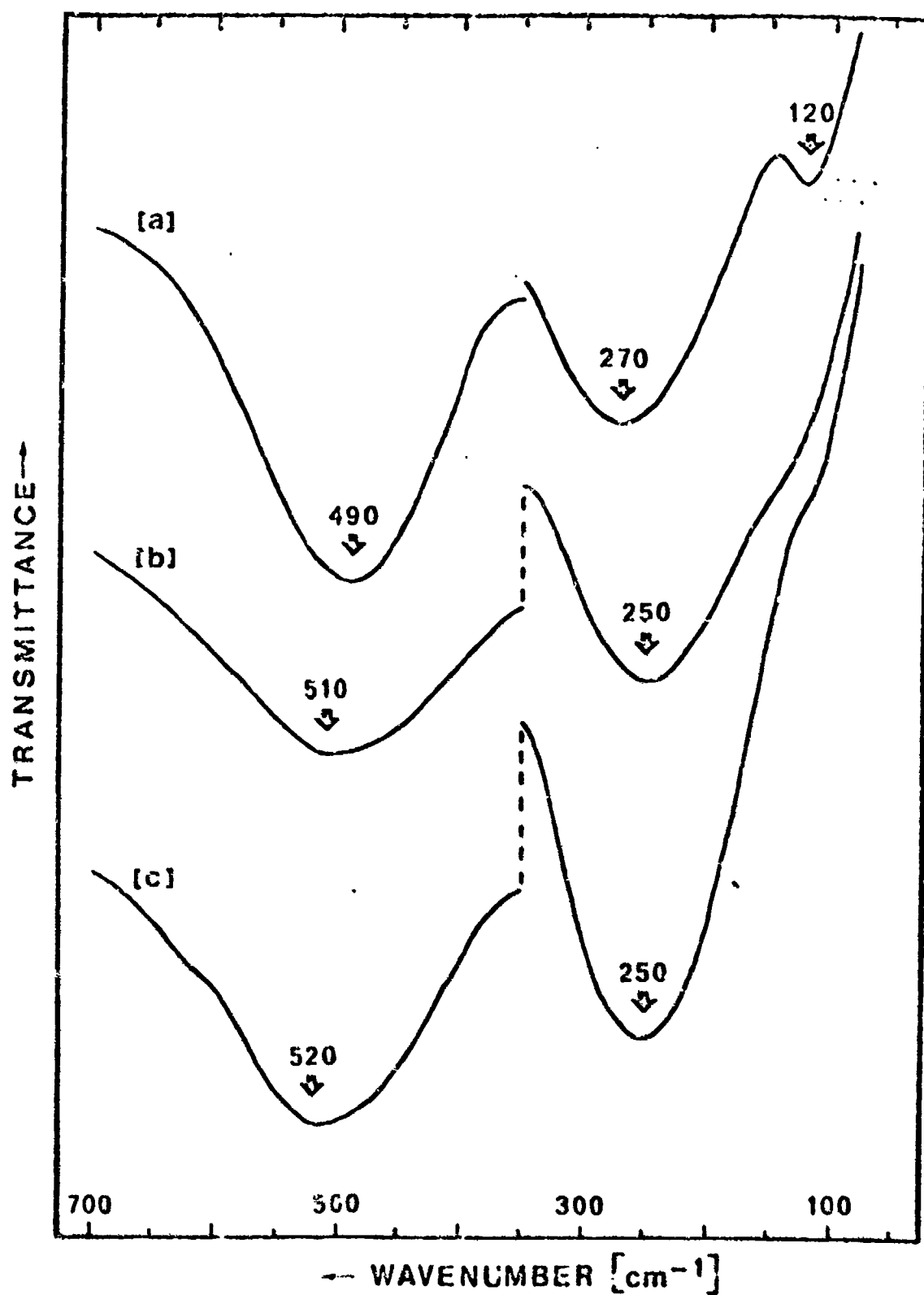


Figure 3 Middle and Far IR Absorption Spectra of (a) 64 ZrF_4 - 36 BaF_2 glass, (b) 67 ZrF_4 - 33 SrF_2 glass and (c) 74 ZrF_4 - 26 BaF_2 glass.

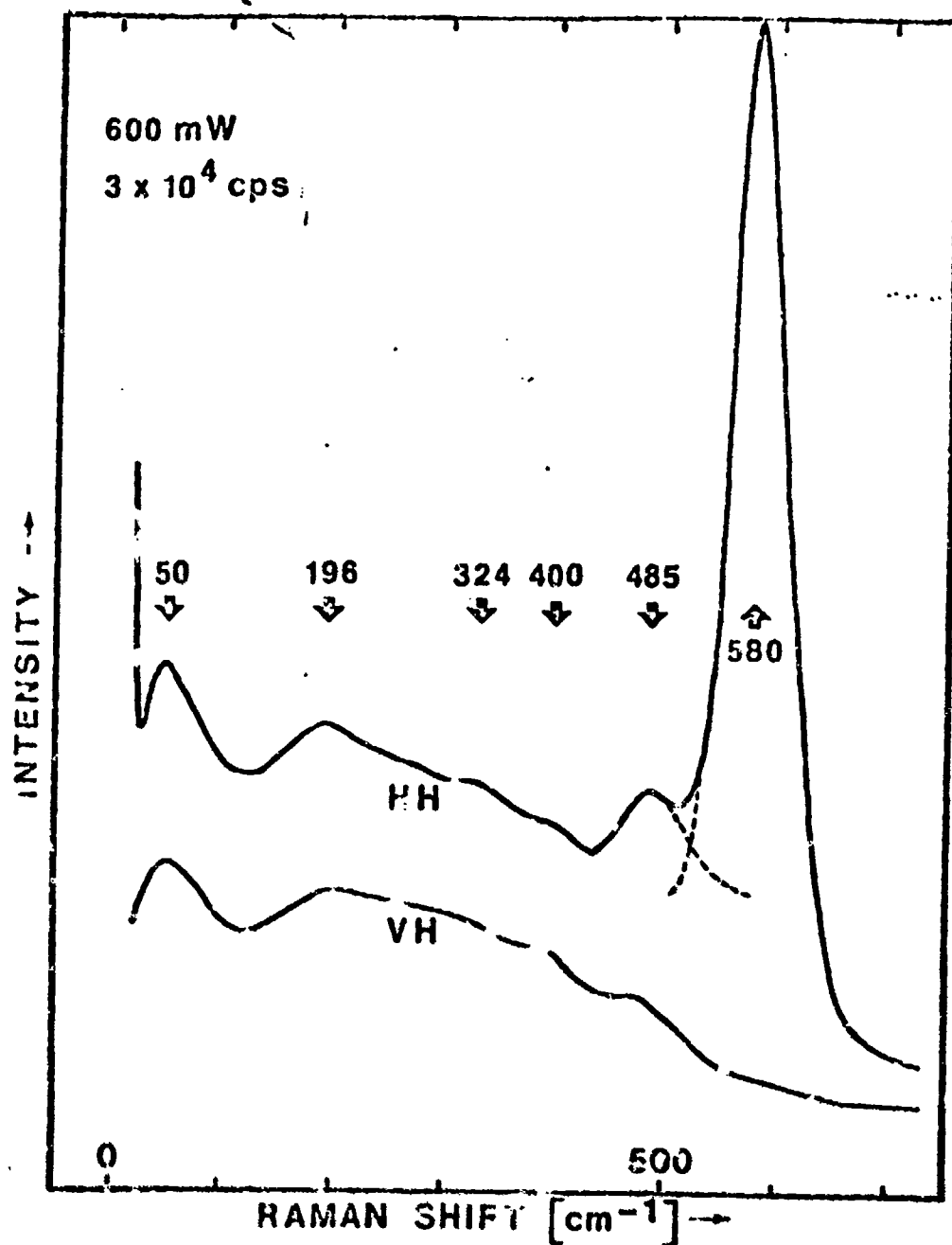


Figure 4 Raman Spectrum of the 64 ZrF_4 - 36 BaF_2 Glass in the Polarized (HH) and Depolarized (VH) Configuration.

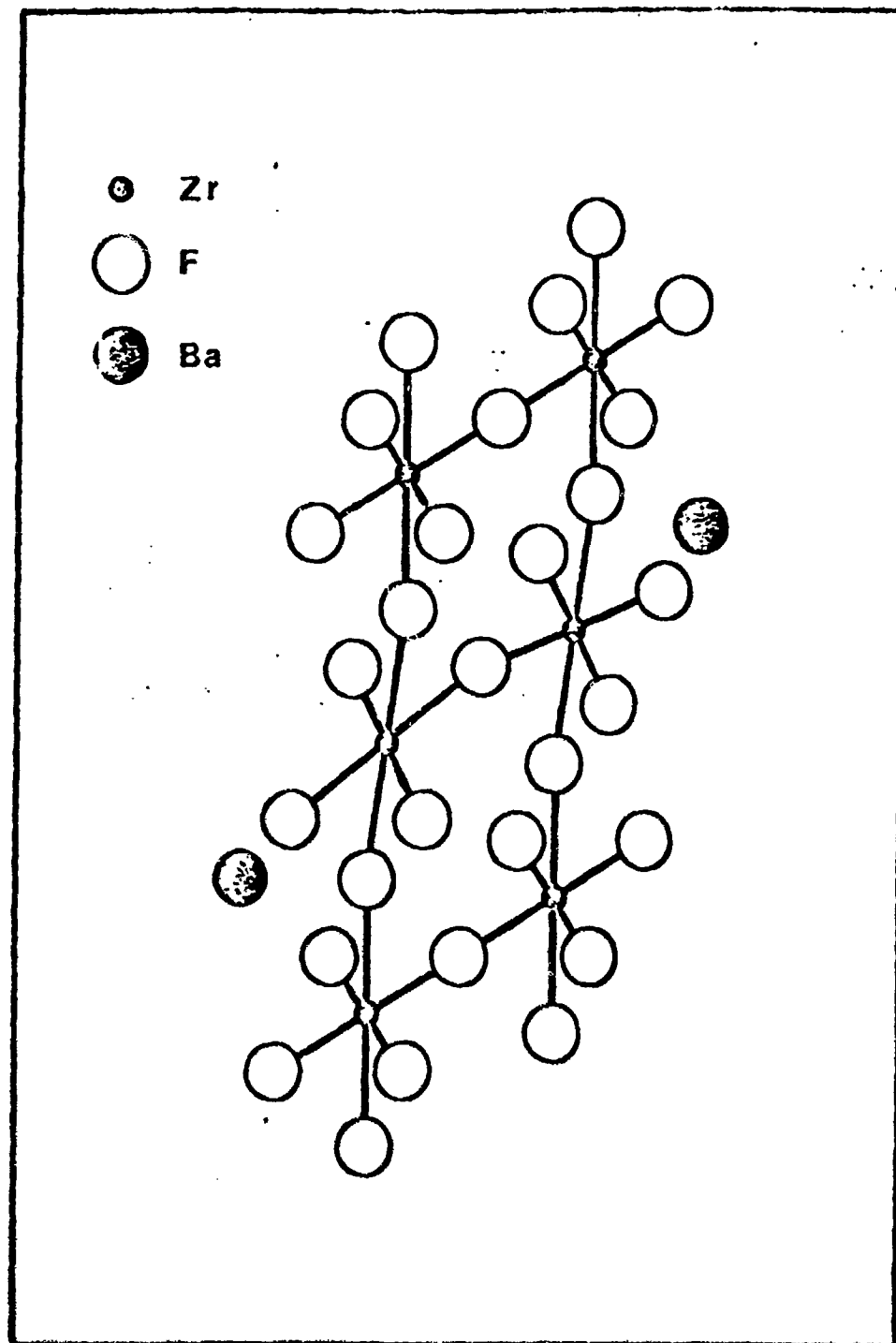


Figure 5 Example of a Double Chain of ZrF_6 Octahedra, in the Structure of Barium Trizirconate Glass $3 \text{ZrF}_4 \cdot \text{BaF}_2$. Such chains are cross-linked by Ba-F ionic bands.

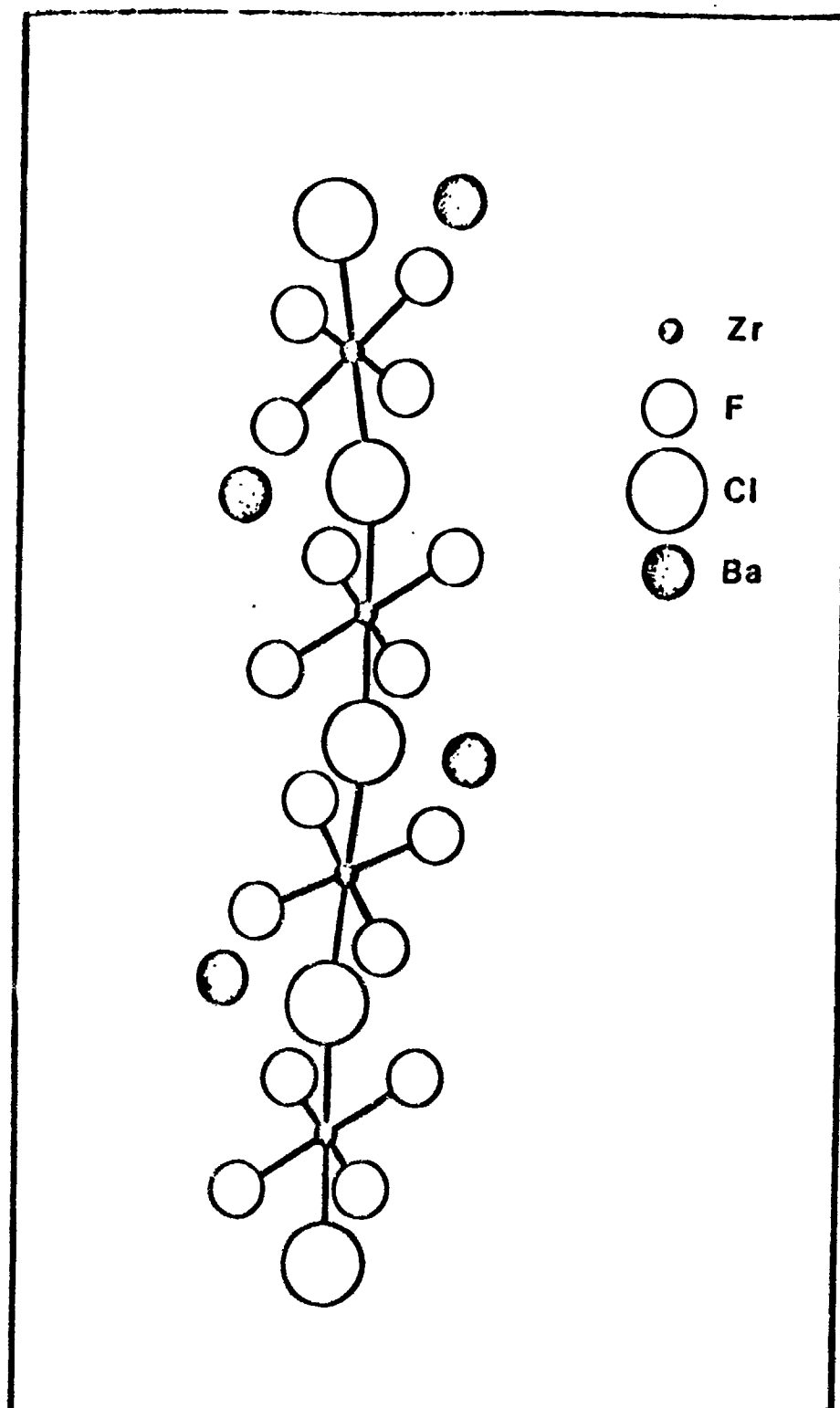


Figure 6 Mixed Halide Chain of ZrCl_2F_6 Octahedra in the Structure of $55 \text{ZrF}_4 - 20 \text{BaF}_2 - 25 \text{BaCl}_2$ Glass. Such chains are cross-linked by Ba-F ionic bonds.

Table 2 Composition and characteristic temperatures of chloro-fluorozirconate glasses

Glass #	Batch composition (mol %)			Analysed composition (mol %)			T_g (°C)	T_{cryst} (°C)
	ZrF ₄	BaF ₂	BaCl ₂	ZrF ₄	BaF ₂	BaCl ₂		
1	55		45	-	-	28	245	265
2	60		40	55	20	25	247	271
3	65		35	-	-	18	261	305
4	70		30	64	26	10	263	321
5	70	10	20	65	28	7	270	327
6	80		20	72	25	3	274	334

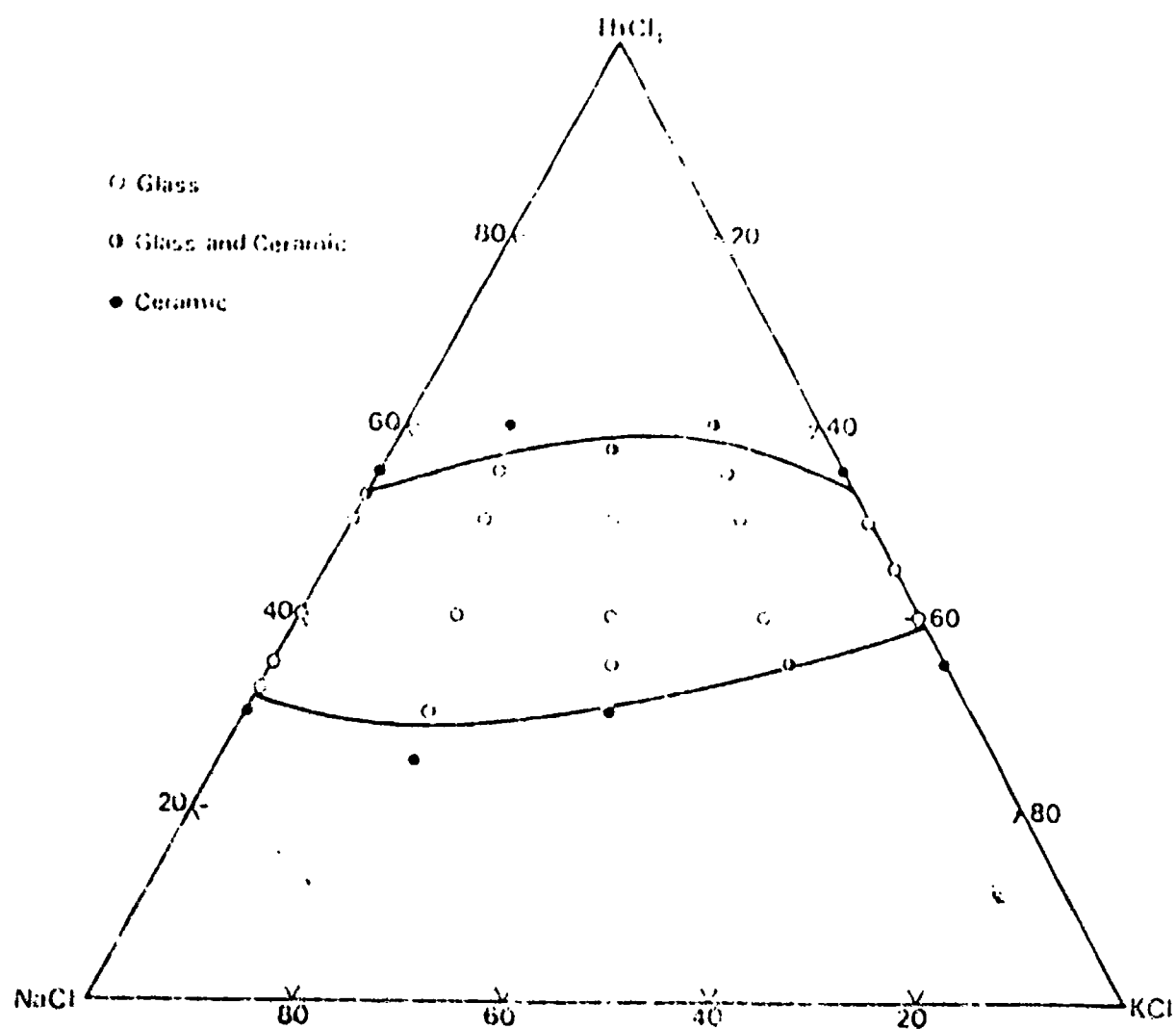


Figure 7 The glass-forming region in ternary system NaCl-KCl-ThCl₄.

glasses will have to be protected by cladding. However, it is likely that by systematic study of glass formation, chemical durabilities can be improved via the addition of other bromides or chlorides.

5. Preparation of Glass Fibers

Two techniques have been evaluated for fiber preparation. The first one involves direct drawing from the melt. The second one involves the preparation of a "pre-form" and subsequent redraw. Because of the low viscosity of currently known glasses, it was decided to test the redraw method. Rods of fluorozirconates were made by casting. Raw materials were distilled. The rods were fitted into a 0.25" i.d. Teflon FEP tubing and redrawn in a dry nitrogen atmosphere. Cladded fibers were successfully drawn with lengths up to 50 feet and diameters down to 50 μ as shown in Figure 8. Experiments have been started to determine the effects of wet atmospheres on the tensile strengths of the fluorozirconate fibers.

6. Effects of Oxygen Content on Glass Properties

Known amounts of ZrO_2 , BaO and La_2O_3 were separately added to distilled fluorides and glasses made with up to 2 weight % oxides. The infrared transmissions were measured as well as other physical properties including viscosity. Although the work is not yet complete, it can be stated at present that small amounts of oxygen can have fairly large effects on the properties of fluorozirconates. A technique was developed which permitted the estimation of oxygen content in fluorozirconates.

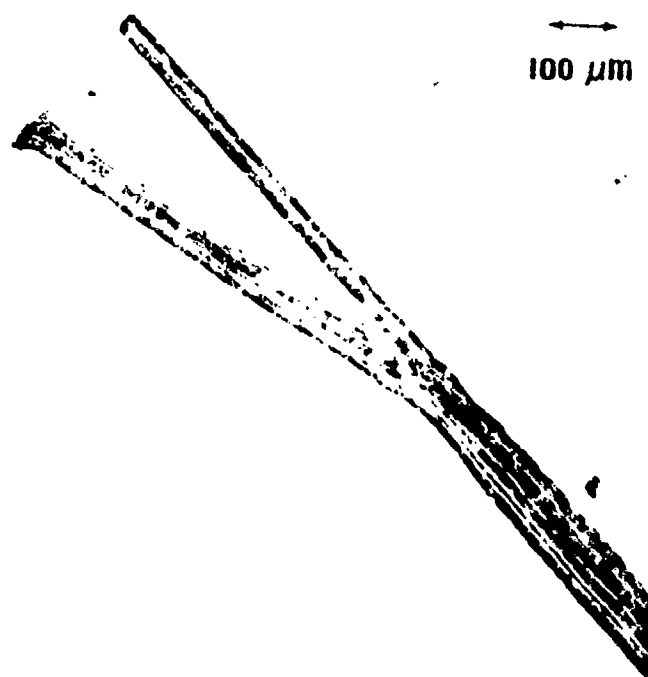


Figure 8 Cladded fluoro-zirconate glass fibers showing stripped cladding of Teflon FEP (left side) and glass fiber core.

III. Research on Impregnated Microporous Silica Glass

A. Background Information

When alkali borosilicate melts of certain compositions are cooled to some temperatures, a peculiar type of liquid-liquid phase separation occurs which exhibits an interconnecting morphology. Such phase separation is known as "spinodal decomposition".^(9,10) One phase is essentially an alkali borate and the other is practically all silica containing about 3% B_2O_3 . When the solidified phase-separated glass is immersed in dilute acids or hot water, the alkali borate phase is preferentially leached away, leaving a "skeleton" of the silica glass.^(11,12) This skeleton is known as microporous glass. The total porosity can exceed 50% and the pore diameters can be controlled by heat treatment to a range from 20 Å to 1000 Å.^(13,14)

Because of the unique microstructure of such fine interconnecting channels microporous glass has been used in reverse osmosis⁽¹³⁾ and for the preparation of enzymes.⁽¹⁵⁾ The channels have been partially coated with carbon to form semiconducting composites⁽¹⁶⁾ and totally filled with metal to give superconductors.⁽¹⁷⁾ The latter example is particularly interesting in that the superconducting transition temperatures can be raised because the metal is in a very fine filamentary state. The micropores in a chemically inert matrix of silica glass offer unique opportunities for studying the behavior of other materials in a fine filamentary state. Further no transparent composites based on microporous glass are known.

Preliminary experiments at UCLA prior to September, 1979, indicated that transparent composites based on polymethylmethacrylate (PMMA) in microporous could be prepared. Secondly, theoretical considerations indicated that the properties of many crystalline solids could be altered if they were impregnated into microporous glass to form fine filaments. There were thus strong justifications to perform research on impregnated porous glass.

B. Research Progress in this Period

1. Polymer-impregnated Porous Glass

Porous glass samples were obtained from Corning Glass Works. Typically the samples were 40% porous and the average pore diameters were 40 Å. Liquid MMA was first impregnated into the micropores and the monomer then polymerized with benzoyl peroxide. The resultant composite was highly transparent in the visible. As a matter of fact the composite was better than window glass in visible transmission. The density of the composite was in-between that of silica glass and PMMA. However, its fracture toughness was considerably higher than that of silica glass whilst its hardness was superior to that of PMMA. The tensile strength of the composite was higher than that of PMMA and window glass. A summary of the important properties measured is given in Table 1. Figure 9 shows the superior visible transmission of this new organic polymer-inorganic glass composite. A number of other liquid monomers were selected for impregnation. The most promising to-date was a copolymer of styrene and dimethyl butadiene.

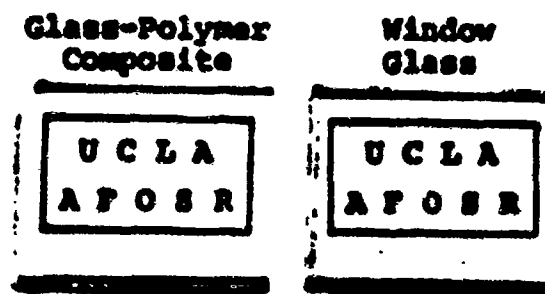


Figure 9 Comparison of transparency between porous glass-polymer composite and window glass.

TABLE 3

Summary of some Important Properties of Porous Glass, PMMA
and Composite

<u>Material Properties</u>	<u>Porous Glass</u>	<u>PMMA</u>	<u>Composite (PG+PMMA)</u>
Modulus of rupture (psi)	8742		19158
Young's modulus (psi)	2.51×10^6	4.75×10^5	3.39×10^6
Poisson's ratio	0.20	0.33	0.22
Density (g/cm ³)	1.446	1.215 ^a 1.188	1.830
Porosity (%)	33.5%		1.9%
Pore diameter (Å)	75		
Hardness (GN/m ²)	0.84	0.22	2.15
Transmittance			92%
Glass temperature (°C)		110 ^a 105	110
Thermal expansion coeff.		7.3×10^{-5}	1.8×10^{-5}
Dielectric constant	5.2	4.9	9.2
Dissipation factor	0.007	0.048	0.038
Fracture energy (J/m ²)	3.33	300	26.65
Toughness (MN/m ^{3/2})	0.30	1.60	1.09

^a PMMA

The fracture toughness of the composite, because of the lower T_g of this polymer, was even superior to that of the PMMA-silica glass composite (1.6 vs 1.1 GN/m²). There is thus good indication that many new polymer-inorganic glass composites can be prepared with interesting and useful properties.

2. Porous Glass Impregnated with Crystals

Three techniques were developed for the impregnation of a variety of inorganic crystalline phases into microporous glass. The first one involves the melt. The second one involves the repeated impregnation and drying of saturated aqueous solutions. The third one involves the repeated impregnation and decomposition of sol-gel liquids. The melting points of the impregnated crystals were determined by DTA and X-ray analysis. Some of the results are shown in Table 4. Large depressions of melting temperatures were observed. A theory has been developed for explaining these melting point depressions. According to this theory, the radius of the microcrystalline particles inside the microporous glass, R , is given by:

$$R = 2 \sigma_{ls} T_m / \rho_s \Delta H_f \Delta T$$

where σ_{ls} = interfacial energy between solid and liquid

T_m = bulk melting point

ρ_s = density of solid

ΔH_f = heat of fusion

ΔT = melting point depression.

Table 4 Melting point depression of various materials
in porous glass.

	Impregnation Method	M.P. (°C) Bulk	M.P. (°C)	ΔT (°C)
NaNO_3	Aq. Soln.	309	262	47
KNO_3	Molten Salt	335	288	47
	Aq. Soln.	"	283	52
	High Pres.	"	295	40
AgNO_3	Aq. Soln.	216	170	46
TlNO_3	Molten Salt	214	177	37
	Aq. Soln.	"	175	39
NH_4NO_3	Molten Salt	175	125	50
	Aq. Soln.	"	123	52
HgI_2	Molten Salt	257	215	42
$\text{K}_2\text{Cr}_2\text{O}_7$	Molten Salt	401	367	34
CuCl	Aq. Soln.	645	565	80
Ag	Aq. Soln.*	961	901	60

* After impregnation by aq. sol. method, heat treated at
500°C - 24 hours.

The average value of R calculated by this equation was 40 Å. The average radius of the pores was found to be 25 Å from experiments. The agreement between theory and experiment was considered to be satisfactory.

Another interesting discovery was that a number of crystals, after impregnation into the microporous glass, no longer exhibit phase transformation at a temperature at which the bulk solid would undergo phase transformation. These include KNO_3 , TlNO_3 , AgNO_3 , HgI_2 , TiO_2 and ZrO_2 . The tentative explanation of this phenomenon is that the average pore size is significantly less than the calculated critical radius necessary for phase transformation. The role of the porous silica glass surface is now being investigated.

B. Preparation of Porous Glass with Larger Pores

Currently, porous glass obtainable from Corning Glass Works has only one pore size, viz. about 40 Å in diameter, and one porosity, viz. 40%. For better understanding of the behavior of composites impregnated into microporous glass and to extend the range of materials which can be impregnated (for instance, large organic molecules), it is desirable to have microporous glass with a wide range of pore size and porosity. We have now been able to develop the capability of preparing microporous glass with average diameters up to 2000 Å and porosity up to 55%. Techniques have also been developed which permitted the accelerated leaching of the borate phase without stress-induced cracking.

IV. Publications in this Period

- "Preparation and Properties of Water-Free Vitreous Beryllium Fluoride", J. of Non-Crystalline Solids 31, 441-445 (1979).
- "Fundamental Condition of Glass Formation in Fluoride Systems," J. Am. Ceram. Soc. 62, 537-539 (1979).
- "The Leaching of Phase-Separated Sodium Borosilicate Glasses," J. Non-Crystalline Solids 31, 377-383 (1979) with A. Makishima and J.J. Hamel.
- "Low Expansion Copper Aluminosilicate Glasses," J. Non-Crystalline Solids 30, 295-292 (1979) with K. Matusita.
- "Improvement of Chemical Durability of High Expansion Phosphate Glasses by Ion Exchange," J. Materials Science 14, 1508-1509 (1979).
- "Electrical Properties of Semiconducting Oxide Glasses," J. Non-Crystalline Solids 32, 91-104 (1979) with L. Murawski and C.H. Chung.
- "Applications of Glass in Electronics," Glass 51, 1-14 (1979).
- "Electrical Properties of Semiconducting Oxide Glasses," Rev. de Chim. Min. 16, 308-327 (1979) with C.H. Chung and L. Murawski.
- "Effect of Ion-Exchange on the Young's Modulus of Glass," J. Non-Crystalline Solids 38, 395-390 (1980) with J. Wakaki.
- "Infrared Absorption and Structure of Chlorophosphate Glasses," J. Non-Crystalline Solids 40, 535-548 (1980) with R. Almeida.
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- "New Methods of Studying Disordered Solids," by J.D. Mackenzie and John Lau, J. de Physique (accepted for publication).
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- "Structure and Properties of Thorium-Fluorozirconate Binary Glasses," by R.M. Almeida and J.D. Mackenzie, Proceedings of XIII Int. Cong. Glass. (Accepted for publication).
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- "Microstructure of Porous Glass by High Resolution Electron Microscopy," J. Non-Crystalline Solids, accepted for publication with Y. Bando.
- "Corrosion of Fluorozirconate Glasses in Water," by M. Liepmann and J.D. Mackenzie, J. Non-Crystalline Solids. (Submitted for publication).
- "Water Resistance of Fluorozirconate Glass," by M. Liepmann and J.D. Mackenzie, J. Non-Crystalline Solids. (Submitted for publication).
- "Effects of Oxygen on the Properties of Fluorozirconate Glasses," by H.F. Hu and J.D. Mackenzie, in preparation.

"Preparation of Porous Glass with Large Pores," by T. Morimoto and J.D. Mackenzie, in preparation.

V. Miscellaneous Achievements

A. Graduate Degrees Awarded

Based on research supported by AFOSR, the following graduate degrees were awarded to graduate students under the supervision of J.D. Mackenzie.

Ph.D. Degrees

C.H. Chung, 1979	J. Wakaki, 1979
R.M. Almeida, 1980	C.C. Liu, 1981

M.S. Degrees

Edward Wu, 1980	Rex C. Claridge, 1980
Monika Liepmann, 1981	Joseph Yuen, 1981
Andrew Ko, 1981	K.C. Chen, 1981

B. Achievements of the Principal Investigator

1. J.D. Mackenzie was Chairman of the Publications Committee of the International Congress on Glass, 1982, and editor of the Proceedings of that Congress.
2. J.D. Mackenzie was organizer of the International Conference on "Frontiers of Glass Science," held in Los Angeles, 1980, and co-editor of the Proceedings.
3. J.D. Mackenzie was invited by the Peoples Republic of China to organize the First International Symposium on Glass, held in Beijing, China, August, 1981 and co-editor of the resulting Proceedings.
4. J.D. Mackenzie was invited to serve on the International Advisory

Committee of the following meetings:

- a. International Conference on Ultrastructure Processing, U. of Florida, February 1983.
- b. International Workshop on Glasses and Ceramics from Gels, Max Planck Institute, Wurzburg, Germany, July, 1983.
- c. International Conference on Glass Science, Tech. U. of Clausthal, Germany, July, 1983.
- d. International Conference on Physics of Non-Crystalline Solids, Montpellier Univ., France, July, 1982.

C. Patents

Three patent disclosures were prepared and submitted to the University of California Board of Patents. Subsequently, these disclosures were transferred to the U.S. Air Force. At present, these disclosures are being processed by the Air Force.

VI. Personnel

During this period, the following had participated and made contributions to the progress reported.

Dr. J.D. Mackenzie, Principal Investigator

Dr. T. Miura, Research Assistant, 1980-81

Dr. T. Takusagawa, Research Assistant, 1979-80

Dr. John Lau, Research Assistant, 1981-82

Dr. N. Tohge, Research Assistant, 1981-82
Dr. R. Almeida, Research Assistant, 1981-82
Mr. H.F. Hu, Research Assistant, 1980-82
Miss M. Liepmann, Research Assistant, 1979-82
Mr. Keith Kadokura, Research Assistant, 1979-82
Mr. C.H. Chung, Research Assistant, 1979
Mr. J. Wakaki, Research Assistant, 1979
Mr. C.C. Liu, Research Assistant, 1979-81
Mr. Edward Wu, Research Assistant, 1979-82
Mr. Andrew Ko, Research Assistant, 1980-81
Mr. Rex Claridge, Research Assistant, 1979-80
Mr. Joseph Yuen, Research Assistant, 1980-82
Mr. F.C. Chen, Research Assistant, 1980-82
Mr. T. Morimoto, Research Assistant 1980-82

In addition a number of undergraduate laboratory assistants were employed to assist in this research program.

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